Asian Journal of Chemistry Vol. 22, No. 6 (2010), 4398-4404

Investigation of Tetra(*p*-carboxyphenyl)porphyrin in Monomer and Aggregation Forms by UV-Vis, ^{1}H NMR, ^{13}C NMR, SEM and Atomic Force Microscopy

RAHMATOLLAH RAHIMI*, FARIBA MOHARRAMI and SEYED HAMED RAHMANPOUR
Department of Chemistry, Iran University of Science and Technology, Tehran, Iran
E-mail: rahmotollah.rahimi@iust.ac.ir

Tetra(*p*-carboxyphenyl)porphyrin (H_2TCPP) was synthesized and characterized by UV-Vis, ^{1}H NMR, ^{13}C NMR and SEM spectroscopy. The porphyrin H_2TCPP aggregated and formed nanorods and nanorings on silica in aqueous acidic solution (HCl). These rods of tetra(*p*-carboxyphenyl)porphyrin were investigated by UV-visible spectroscopy and atomic force microscopy in aqueous acidic solution.

Key Words: Tetra(*p*-carboxyphenyl)porphyrin, Spectral studies.

INTRODUCTION

Porphyrins are perhaps best known for their biological functions and coordination chemistry[1]. The chemical and physical properties of porphyrins continue to attract considerable interest, because of the vital role of some of these species playing in biological processes. Studies have shown that some of *meso*-substituted porphyrins dimerize in aqueous solution[2,3]. The tendency of porphyrins to aggregate is also important because of its significant biological role[4,5]. The properties of the variety of *meso*-substituted water-soluble porphyrins are dependent on the charge type of the periphery of the molecule. Porphyrins having negative charges at the periphery ($TPPS_3$ and TCPP) are considerably more basic and have much greater tendency to aggregate than those having positive charges at the periphery (TPyP and TMPyP). Metallo derivatives of TCPP have also greater tendency to aggregate than those of TMPyP[6].

The nano *tetrakis*(4-sulfonatophenyl)porphyrin aggregation was characterized by Rahimi *et al.*[7]. In nature, assemblies of porphyrin derivatives are done by photosynthetic plants and organisms through their high capabilities in light-harvesting process[8].

EXPERIMENTAL

Tetra(*p*-carboxyphenyl)porphyrin (H_2TCPP) was synthesized by the method of Adler[9], the amount of 1.05 g pyrrole with 2.3 g of 4-carboxy benzaldehyde was refluxed in 50 mL of propionic acid for 2 h. The Purification of product was done by flash chromatography and characterized by ^{1}H NMR, ^{13}C NMR, SEM and UV-visible spectroscopy in NaOH aqueous solution with pH 9. Aggregation of H_2TCPP in HCl at pH 1 was investigated by UV-visible and atomic force microscopic spectroscopy. In preparation of sample for atomic force microscopy results, the silica substrate was cleaned with methanol and then were placed for 2 to 6 min in aqueous acidic solutions of 5×10^{-5} M TCPP.

RESULTS AND DISCUSSION

The absorption spectra of the solution of H_2TCPP in NaOH at pH 9 and in HCl at pH 1 are shown in Figs. 1a and b. The solution of 1×10^{-5} M H_2TCPP at pH 9 is pink and exhibits five absorption bands; one band in Soret at 414 nm (3.5×10^5 M^{-1} cm^{-1}) and four Q bands at 517, 554, 579 and 634 nm with the molar absorption coefficients of 1.2×10^4, 6.5×10^3, 5.2×10^3 and 3.3×10^3, respectively.

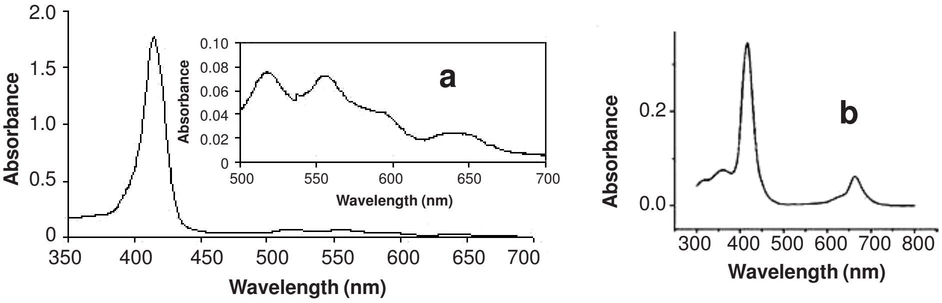


Fig. 1. (a) Absorption of TCPP at pH = 9; (b) aqueous HCl at pH 1

The solution of 1×10^{-5} M H_4TCPP^{2+} at pH 1 with HCl is green colour, exhibits two absorption bands; one Soret band at 420 nm and the other Q band at 670 nm. The different absorptions of TCPP in HCl compared with basic solutions is because of H-aggregation of TCPP in HCl and protonation of pyrrole rings of porphyrin in acidic solution.

The addition of two hydrogens by HCl on the nitrogen atoms of the free base porphyrin, increase the ring symmetry from D_{2h} to D_{4h}. In general, a more symmetrical molecule gives a simpler spectrum. The 22 π-electron orbitals in the free-base porphyrin are the basis of orbitals combined to create the π molecular orbitals of the porphyrin ring. Since the point group is D_{2h}, thus the reducible representation are as follows:

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
For TCPP	22	0	-2	0	0	-22	0	2

which reduces to 5 B_2g + 6 B_3g + 5 Au + 6 B_1u. None of these states are degenerate. After metalation the symmetry is D_{4h}, as all four nitrogens are equivalent. The resulting basis set consists of the 24 p_z orbitals.

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
For H_2TCPP^{2+} in HCl	24	0	0	-2	-2	0	0	-24	2	2

which reduces to 6Eg + $3A_1u$ + $3A_2u$ + $3B_1u$ + $3B_2u$. With the increased symmetry many of the molecular orbital are now doubly degenerate, which accounts for the reduction in the number of peaks in the visible spectrum. In Fig. 2, p_z orbitals of TCPP and H_4TCPP^{2+} are showed by star.

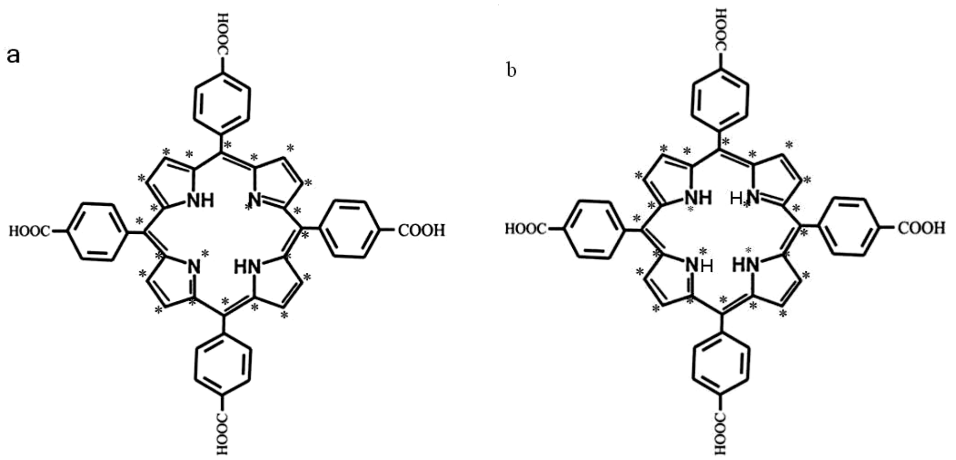
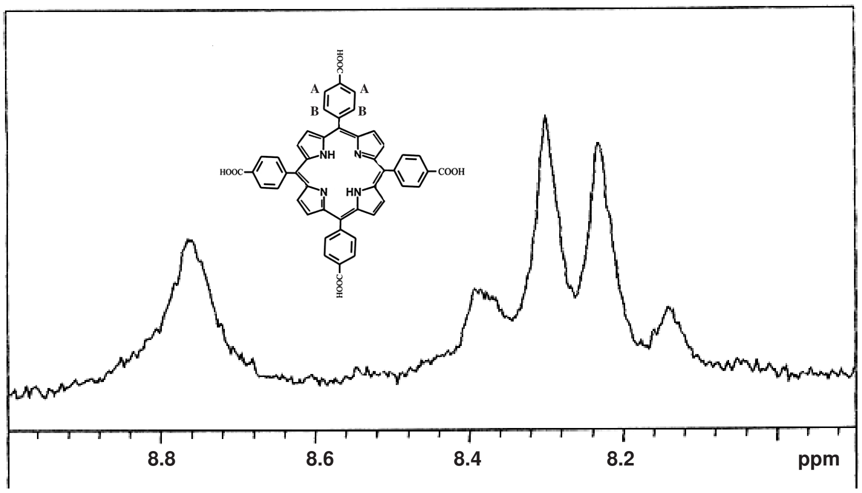


Fig. 2. The position of the p_z orbitals used as a basis of group theory. (a) Free-base H_2TCPP. (b) H_4TCPP^{2+}. *p_z orbital

Fig. 3a shows ^1H NMR and ^{13}C NMR of free base H_2TCPP, the peak at 8.8 ppm is for 8 hydrogens of β-pyrrole. This peak shows that eight hydrogens of β-pyrrole are equal because of tautomerization of 2 amine hydrogens of H_2TCPP ring. By reducing the temperature, this peak was splited. The peaks in region between 8.4-8.2 ppm belongs to A and B hydrogen that shown in Fig. 3a. The A and B hydrogens are not equal, but they split each other in two doublet peaks.



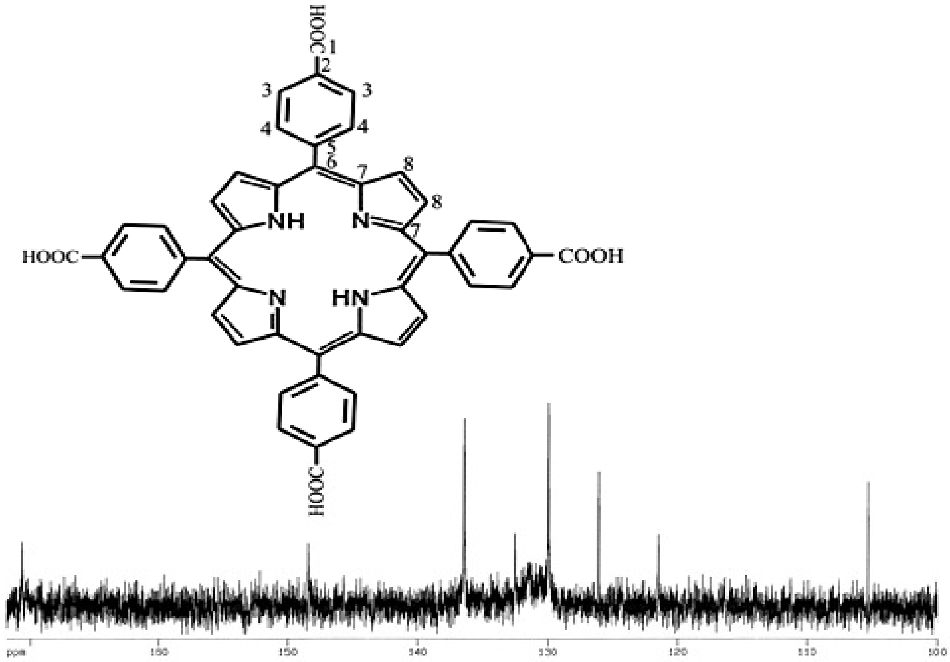


Fig. 3. (a) ^{1}H NMR 90 spectrum. (b) ^{13}C NMR spectrum of H_2TCPP

Aromatic carbons are in region 120-140 ppm that are for four carbons: 2, 3, 4, 5. Carbon of COOH group is showed at 170.658 that is carbon 1, the peaks at 126 and 105 are for 7 and 8 carbons, respectively.

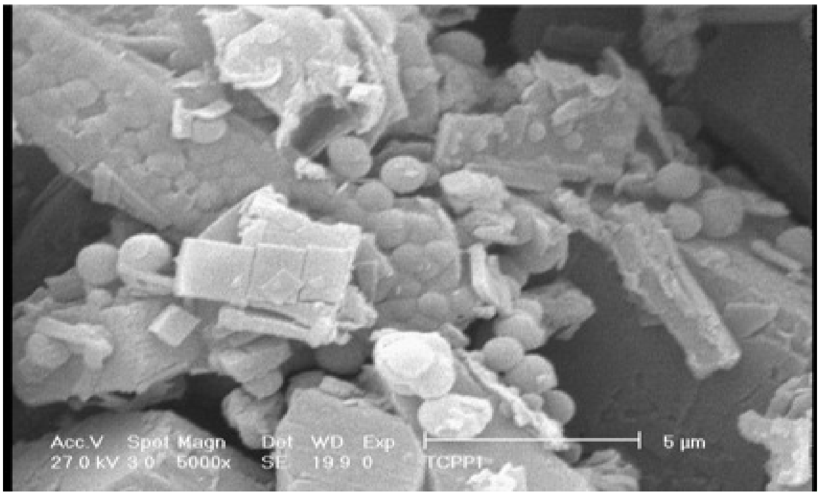


Fig. 4. SEM image of H_2TCPP

The SEM photograph in Fig. 4 shows π interaction of intra molecular. The atomic force microscopic images of H_4TCPP^{2+} on silica in aqueous solution of HCl at pH = 1, confirms the existence of nanostructures in the presence of Cl^- ions. These images shows rings and partial rings of various diameter and height of nanorods for H_4TCPP^{2+} deposited from aqueous HCl on to silica substrate. The Fig. 5 shows the height of nanostructures for H_4TCPP^{2+} on silica is 600 nm and we can also see in Fig. 6, the shape of rings as a result of H-aggregation of H_4TCPP^{2+} in the form of nanostructure.

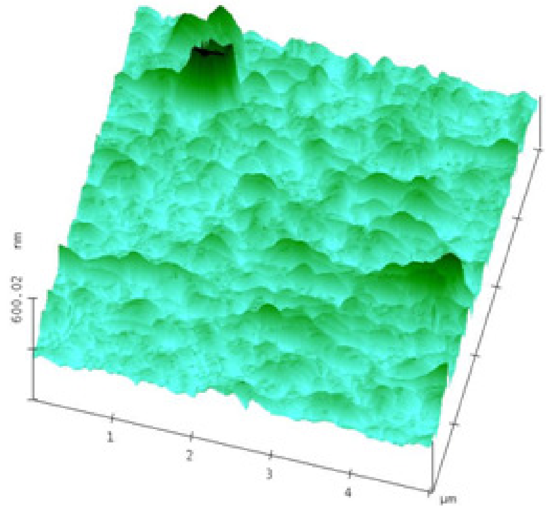
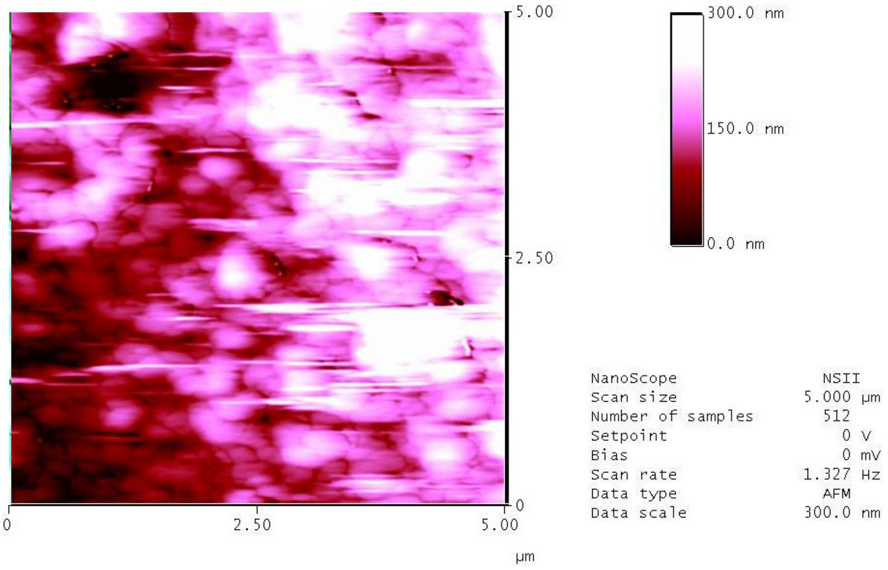


Fig. 5. Atomic force microscopic image of H_4TCPP^{2+} sample on silica aqueous HCl solution (pH = 1)



```
NanoScope            NSII
Scan size            5.000 μm
Number of samples    512
Setpoint             0 V
Bias                 0 mV
Scan rate            1.327 Hz
Data type            AFM
Data scale           300.0 nm
```

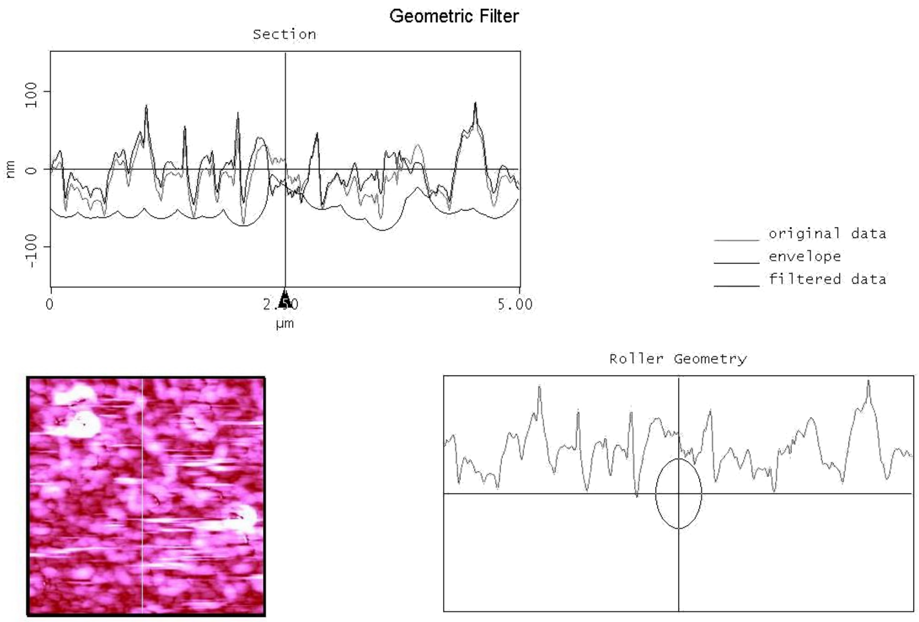


Fig. 6. Atomic force microscopic image of nanorods for H_4TCPP^{2+}

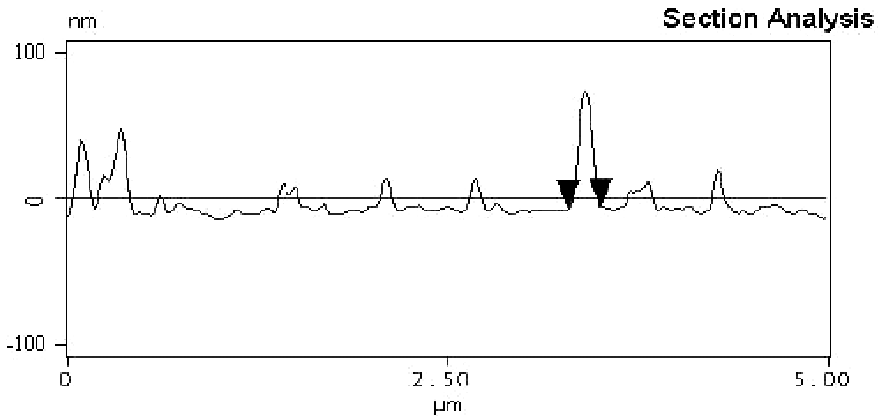


Fig. 7. Atomic force microscopic section analysis of H_4TCPP^{2+} samples on silica

Conclusion

In this work, H_2TCPP was synthesized and characterized by ^1H NMR, ^{13}C NMR and SEM UV-Vis spectroscopy. The aggregation of H_4TCPP^{2+} in aqueous acidic solution at pH = 1 is confirmed by UV-Visible spectroscopy and atomic force microscopy. The nanoparticles obtained from H_4TCPP^{2+} in aqueous HCl solution was observed by AFM to have structures such as nanorouds which are microns in length and about 600 nm in height.

REFERENCES

1. B. Karami, M. Montazerozohori, M. Moghadam, M.H. Habibi and K. Niknam, *J. Turk. Chem.*, **29**, 539 (2005).
2. R.F. Pasternack, P.R. Huber, P. Boyed, G. Engasser, L. Francesconi, E. Gibbs, P. Fasella, G.C. Venturo and L. deC. Hinds, *J. Am. Chem. Soc.*, **94**, 4511 (1972).
3. R.F. Pasternack, L. Francesconi, D. Raff and E. Spiro, *Inorg. Chem.*, **12**, 2606 (1973).
4. J.E. Falk, Porphyrins and Metalloporphyrins, Elsevier, New York (1964).
5. R.G. Clayton, in eds.: L.P. Vernon and G.R. Seely, The Chlorophylls, Academic Press, New York (1966).
6. K. Pyrzynska and K. Kilian, *J. Sep. Sci.*, **29**, 282 (2006).
7. R. Rahimi, M. Jeddi and S.M.R. Ravanfar, *Asian J. Chem.*, **21**, 3988 (2009).
8. M. Dulrr, S. Rosselli, A. Yasuda and G. Nelles, *J. Phys. Chem. B*, **110**, 21899 (2006).
9. A. Longo, F.R. Adler, F.R. Longo, J.D. Finarelli, J. Goldmacher, J. Assour and L. Korsakoff, *J. Org. Chem.*, **32**, 476 (1967).

(*Received*: 1 August 2009; *Accepted*: 12 February 2010) AJC-8421